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Synthesis of a renewable sourced thermotropic polyester with 2,5-furandicarboxylic acid

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ABSTRACT

SYNTHESIS OF A RENEWABLE SOURCED THERMOTROPIC POLYESTER WITH 2,5-FURANDICARBOXYLIC ACID

by
Alicia Marie Marguerite Hurst

With the rapid depletion of non-renewable sourced materials, unpredictable fluctuations in the prices of fossil fuels, and increased environmental awareness the need to develop biobased materials grows ever more desperate. Furan derivatives sourced from hexoses provide a promising solution for replacing petrochemical based materials. One furan derivative in particular, 2,5-furandicarboxylic acid (FDCA), is especially promising due to its structural similarity to terephthalic acid and potential for use in the production of polyesters similar to PET, PPT, and PBT. This study investigated the synthesis, thermal and liquid crystalline properties of a totally renewable sourced thermotropic polyester based on FDCA. Fructose was converted to 5-hydroxymethylfurfural, which was then used to synthesize the FDCA monomer. A polycondensation reaction involving 4-hydroxybenzoic acid, hydroquinone, and FDCA was subsequently carried out to produce a random mesogenic polyester. ATR-FTIR spectroscopy was used to analyze the backbone structure of the polymer. Thermal analysis performed on a DSC demonstrated a glass transition temperature and overlapping nematic and isotropic melt phases, suggesting that the polyester is biphasic. This biphasic characteristic was supported by the observations made through an optical microscope with crossed polarizers. The polymer demonstrated both isotropic properties and birefringence with the formation of nematic droplets in the melt. These results exemplify the potential for FDCA derived polyesters to replace their petrochemical derived counterparts.

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by
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I dedicate this thesis to Korey Rose, for without his unwavering support and unconditional love none of this would have been possible.

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LIST OF SYMBOLS

HMF	5-Hydroxymethyfurfural
FDCA	2,5-Furandicarboxylic Acid
TPA	Terephthalic Acid
PET	Polyethylene Terephthalate
PBT	Polybutylene Terephthalate
PPT	Polypropylene Terephthalate
PEF	Polyethylene 2,5-Furandicarboxylate
˚ C	Degree Celsius
H_2SO_4	Sulfuric Acid
H_3PO_4	Phosphoric Acid
HCl	Hydrochloric Acid
DMSO	Dimethyl Sulfoxide
%	Percent
M	Molarity (moles/liter)
NH_4Cl	Ammonium Chloride
TEMPO	2,2,6,6-Tetramethyl-piperidin-1-oxyl
LC	Liquid Crystal
LCP	Liquid Crystal Polymer
WAP	Wholly Aromatic Polymer
T_m	Melting Point
HBA	4-Hydroxybenzoic Acid
p-HBA	para-Hydroxybenzoic Acid

LIST OF SYMBOLS
(continued)

m-HBA	meta-Hydroxybenzoic Acid
T_g	Glass Transition Temperature
IA	Isophthalic Acid
PHMBF	poly (1,4-phenylbismethylene 2,5 furancarboxylate)
PBHMF	poly (2,5-furandimethylene 2,5 furandicarboxylate)
PHQF	poly (1,4-phenylene 2,5-furandicaroxylate)
MW	Molecular Weight (grams/mole)
NMR	Nuclear Magnetic Resonance
TMS	Tetramethylsilane
NaOH	Sodium Hydroxide
$NaHSO_3$	Sodium Bisulfate
$KMnO_4$	Potassium Permanganate
NaOAc	Sodium Acetate
HQ	Hydroquinone
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
mL	Milliliter
ppm	Parts Per Million
mmol	Millimole
mol	Mole

LIST OF DEFINITIONS

Acidic	The condition of water or soil which contains a sufficient amount of acid substances to lower the pH below 7.0.
Alkaline	The condition of water or soil which contains a sufficient amount of alkali substances to raise the pH above 7.0.
Aromatic	A compound with a planar benzene ring.
Birefringence	The optical property of a compound that results in the refraction of polarized light.
Furan	A five-membered aromatic ring with four carbons and an oxygen atom.
Liquid Crystal	A compound with one or more highly ordered liquid phases.
Lyotropic	A compound with liquid crystal properties that are induced when the compound is dissolved in a solvent.
Mesogen	A compound the displays liquid crystal properties.
Moiety	A part of functional group of a molecule.
Polycondensation	A chemical condensation the results in a high molecular weight compound.
Standard	A physical or chemical quantity whose value is known exactly, and is used to calibrate or standardize instruments.
Thermotropic	A compound with liquid crystal properties that are thermally induced.

CHAPTER 1

INTRODUCTION

Recently, the amount of research focused on developing renewably sourced polymers has grown exponentially. At the beginning of the 20th century, much of the scientific community was working towards finding ways of converting biomass to fuel. By the 1960's, however, petroleum derivatives had almost completely replaced biobased chemical products.[1] It is only now, charged with an ever growing demand for quickly depleting geological resources that the focus has shifted back towards renewable sources. This recent increase has not only been motivated by environmental concerns, but also by social and political concerns including unpredictable fluctuations in the price of crude oil and a shift in European and United States legislation towards environmental conservation and renewal [2-4]. The emergence of the biorefinery vision of the 21st century has spawned a large influx of publications addressing these concerns. For example, Viela et al. thoroughy outlines the most recent advances made toward developing biofules and biomaterials [5], as does Ragauskas et al. [1]. Similarly, Miller has compiled a themed collection for the scientific journal, *Polymer Chemistry* entitled,"Sustainable Polymers: Replacing Polymers from Derived Fossil Fuels" [6]. All of this attention has lead to the development of what Gandini refers to as a "novel realm of sustainable macromolecular science" [7]. Within this realm of sustainable macromolecular science, furan based molecules have received more attention than others. One such furan is 5-hydroxymethulfurfural (HMF). HMF is a nonpetroleum monomer precursor that is readily accessible from polysaccharides like glucose and fructose [8]. Unfortunately, due

to its propensity to degrade in even mild environmental conditions, HMF is difficult to store. Therefore, it is more practical to store the molecule in the form a derivative. [9]

HMF derivatives include a wide array of furan monomers that when polymerized, produce materials comparable to those generated from fossil resources [8]. These monomers are synthesized through the introduction of functional groups such as carboxyl, hydroxyl, amino, and isocyanoate groups. In particular, the HMF derivative, 2,5-furandicarboxylic acid (FDCA), has received a considerable amount of attention [10]. FDCA is not only one of the most stable monocyclic furan derivates [9, 11], it also has a key structural feature in that it resembles its aromatic counterparts, making it a potential candidate for synthesizing polymers; specifically polyesters and polyamides [8]. Perhaps most significantly, FDCA very closely resembles terephthalic acid (TPA): a petrochemical used in high performance polyesters namely, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polypropylene terephthalate (PPT) [2, 11]. As such, FDCA derived polyesters have the potential to replace the traditionally petrochemical based products with new biobased materials and thusly have increasingly garnered more attention from researchers in recent years.

The first reported FDCA containing polyester is cited in a 1946 patent for British Celanese where by the inventors prepared polyesters by polycondensing glycols with dicarboxylic acids [12]. Later, a 1958 publication by Osaka University describes the synthesis of polyethylene 2,5-furandicarboxylate (PEF) using a lead catalyst. The product was reported to have a melting point between 220 ˚C and 225 ˚C and to readily form /fibers from the melt. The authors also reported on the tri-, tetra-, penta-, and hexamethylene analogs of the polymer. [13] These studies, however, were limited and

provided very few characterization details. It was not until the 1970's when Moore and Gandini began to research furan polyesters in detail and publish their findings that the full versatility of the furan based polyesters began to be understood [14]. Further research on this polyester, however, was curtailed by the previously described shift in focus towards petrochemical based products. Other than a single review in 1997 [15], FDCA only received scattered mentions in reviews on wider domains [7, 9, 16-18]. That is, until recently when FDCA research experienced a sort of experimental revival. As described in a 2015 review by Sousa et al., the last 10 years have seen an exponential increase in the amount of research published and patents procured for FDCA derived polymers [2]. A quick search on the ISI Web of Knowledge for citations regarding FDCA provides a graphical view of this rapid expansion:

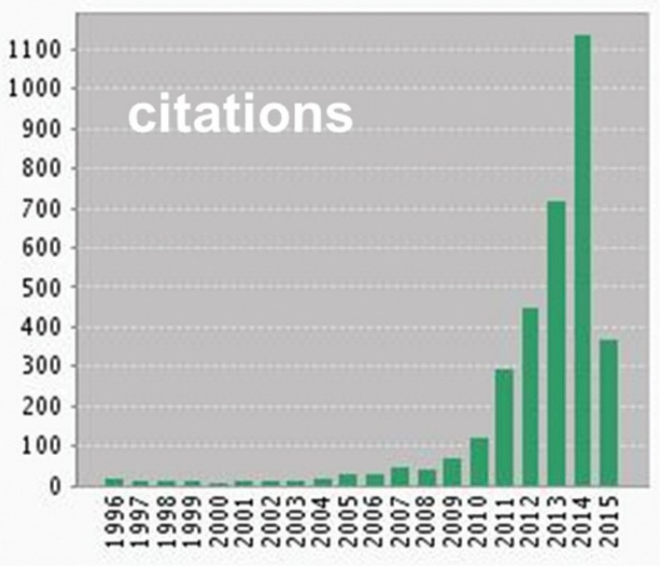


Figure 1.1 Trend evolution for citations involving FDCA [19].

Most of the FDCA research being conducted is focused on the furanic-aliphatic polyester and polyamide family. Though, there is also work being done on furanic-aromatic and non all aromatic polyesters. This work aims to prepare novel materials with

desired characteristics such as thermal, mechanical, and liquid crystalline properties [2]. In congruence with this trend, the objective of this thesis is to synthesize a fully renewable sourced polyester with FDCA that demonstrates liquid crystalline behavior.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Synthesis of 2,5-Furandicarboxylic Acid

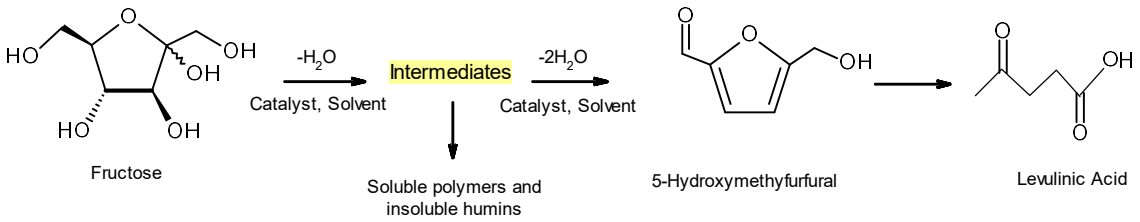
2.1.1 Dehydration of Fructose to 5-Hydroxymethylfurfural

The first recorded research involving HMF is described in two independent 1895 publications that reported on the synthesis and reactions of "oxymethyfurfurol" [20, 21]. It was not until 1944 that the modern procedure for synthesis of HMF was developed by Hawthorn and Jones [22]. Since then, increasingly more research has focused on the production of HMF from hexoses; especially fructose and glucose. In 1951, Newton et al. published the first review of the topic [23], followed by Moye et al. in 1963 who reviewed the synthetic methods and industrial applications of the molecule [24]. Two basic reviews by Gaset published in the early 1980's [25, 26] were followed by more exhaustive reviews by Kuster, Van Dam et al., and Cottier and Descotes. These publications reported on all of the parameters that can affect the homogenous acid-catalyzed dehydration of hexose to HMF in an aqueous solution [27-29]. Focus on HMF has continued to expand so that by 2001 over 1,000 papers had been published on the topic. More recently, this expansion has only continued to grow, with 90 articles on HMF published in 2010 alone [30]. A complete summary of the immense volume of research regarding this topic is outside the scope of this thesis, but readers are directed to Lewkowski, Moreau et al., Tong et al, Rosatella et al., and Van Putten et al. for the most recent comprehensive reviews [30-34].

Nearly 100 liquid/solvent inorganic and organic acid compounds have been found to act as catalysts for the synthesis of HMF. The least expensive and subsequently most common of these catalysts include sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and hydrochloric acid (HCl). Additionally, many solid acid compounds have been shown to catalyze the formation of HMF. These solid catalysts have several advantages over liquid catalysts in that they facilitate the separation of the product, are recyclable, remain active at high reaction temperatures, and demonstrate a higher selectivity for HMF. Examples of solid acid catalysts include metal catalysts, H-form zeolites, ion exchange resins, vanadyl phosphate, and zirconia [33]. Ionic liquids have also been shown to successfully function as both solvents and catalysts. These liquids are of particular interest as they are more environmentally friendly due to their low vapor pressure and recyclability [35]. Regardless of the preferred catalyst, the dehydration of hexose to HMF is proven to be a complex reaction with multiple side reactions that influence the efficiency and yield of the product [31].

Studies show that the synthesis of HMF proceeds through a triple dehydration of hexoses with literature strongly supporting the theory that the first dehydration is the limiting step [34]. This reaction can be carried out in either aqueous or non aqueous solutions. Regardless of the solvent, however, the reaction is extremely complicated and prone to side reactions with decomposition into levulinic acid and cross polymerization having the greatest impact on lowering the product yield (see scheme 1). Van Dam and Cottier reported that in both aqueous and non aqueous systems, the reaction produced up to 37 different products with reactions in aqueous solutions promoting the degradation of HMF and cross polymerization occurring in both solvent types [31]. This cross

polymerization produces soluble polymers that are difficult to isolate and insoluble brown to black humins [27]. Additional challenges arise when attempting to isolate HMF as the distribution coefficient between organic and aqueous phases is not favorable [30]. Much research has focused on trying to determine the dehydration mechanism in hopes that a better understanding of the reaction will shed light on a more selective pathway [27, 28, 36].



Scheme 2.1 Triple dehydration of fructose to HMF with degradation into levulinic acid and intermediate cross polymerization producing soluble polymers and insoluble humins.

The dehydration of hexoses to HMF is found to proceed through at least two intermediates: $C_6H_{10}O_5$ and $C_6H_5O_4$ [27]. Exactly how the reaction proceeds through these intermediates, though, is still under debate. There are two proposed mechanisms: one that assumes the transformation of cyclic intermediates and another that proceeds via acyclic intermediates. A recent NMR study of the mechanism by Akein et al. supported the proposed cyclic intermediate pathway [37]. The findings of another study by Amarasekara et al. identified the intermediate (4R, 5R)-4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde, which was also consistent with the cyclic dehydration mechanism. In this study, the researchers analyzed the dehydration of fructose to HMF in dimethyl sulfoxide (DMSO) without the inclusion of a catalyst. Their results showed that the DMSO acted as both the solvent and the catalyst [38]. These results are especially

promising since using DMSO as the solvent has been shown to significantly repress the formation of byproducts [30].

Similarly, Musau et al. demonstrated conversion of fructose to HMF without a catalyst at 150 ˚C in DMSO with 92% selectivity for HMF. They reported that the optimum conversion was achieved with a large excess of DMSO (8:1). The researchers suggest that this excess is necessary because DMSO first associates with the fructose and then generates water, thereby reducing the amount of DMSO available for the dehydration reaction [39]. Brown et al. also investigated the dehydration of fructose to HMF in DMSO without a catalyst, reporting complete conversion of the reactants after 16 hours at 100 ˚C. They also found that the use of a base catalyst inhibited the formation of HMF while an acid catalyst promoted HMF formation. Their results show complete conversion of the reactants after 45 minutes at 100 ˚C with 0.1 M ammonium chloride (NH_4Cl) as a catalyst [40]. These studies demonstrate promising results with potential applications for large scale production of HMF.

2.1.2 Oxidation of 5-Hydroxymethylfurfural to 2, 5-Furandicarboxylic Acid

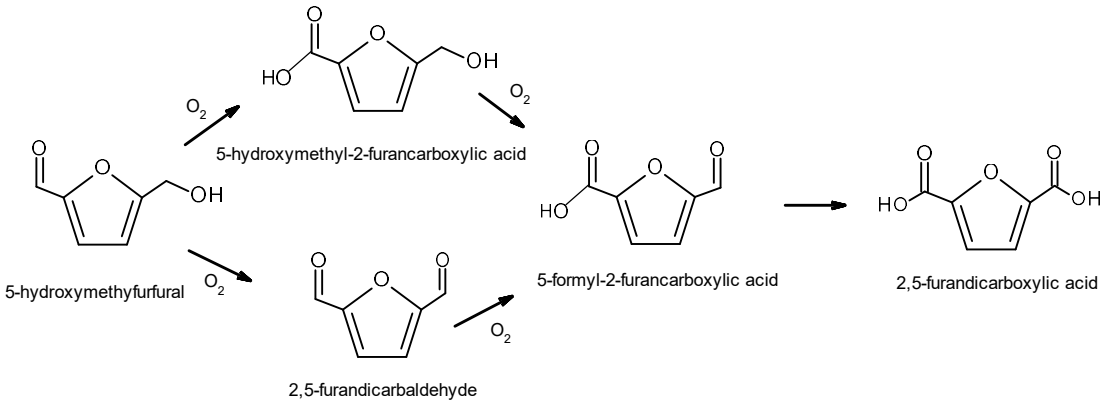
The first work describing the synthesis of FDCA was published by Fittig and Heinzelman in 1876. In this study, the authors reportedly produced FDCA through dehydration of galactoric acid with fuming hydrobromic acid [41]. A second publication in 1888 by Sohst and Tollens described a similar process, but instead used a saccharic acid isomer for the reaction [42]. The first reported use of HMF and its derivatives to derive FDCA was published in 1899 by Fenton and Gostling [43]. A later publication by Hoehn describes the condensation of glyoxal with dimethyl diglycolate with sodium methoxide [44]. This momentum in researcher focused on biobased materials continued into the

1960s as evidenced by the US patent obtained by Atlas Chemical Industries Inc describing the oxidation of HMF to FDCA by reacting HMF with gaseous oxygen and a platinum or palladium catalyst with a molar excess of an alkali metal hydroxide such as copper or gold oxide [45]. At this time, however, petrochemical based materials were gaining traction and the industry focus shifted away from biobased materials.

The early 21st century saw the emergence of biorefinery concepts and with it, publications such as Ragauskas' "The Path Forward for Biofuels and Biomaterials." Ragauskas' publication provides a metaphorical roadmap for the transition from non-renewable to renewable resources [1]. This inception of the biorefinery era was propelled forward with the highlight of certain biomass obtainable chemicals in a key study released by the US National Renewable Energy Laboratory in 2004 [2]. Among the highlighted chemicals were 12 sugar-based monomers including FDCA, which was cited as a desirable potential analog for use in polymers that could replace PET and PBT [46]. This renewed emphasis on biobased materials reinvigorated research attempts to find the best method for synthesizing FDCA.

Oxidation of HMF to FDCA can be achieved using several different methods (see scheme 2). Traditional strong oxidation reagents in stoichiometric concentrations have long been known to successfully produce FDCA from HMF. Such reagents include chromate, dichromate, and permanganate. US patent 20070232815 describes just such a method in alkaline aqueous solution under mild reaction conditions [47]. Though effective, these methods are not favorable on a large scale due to the large volumes of highly toxic metal waste produced [48]. Thusly, researchers have investigated other avenues to complete the oxidation reaction. Several groups have successfully oxidized

HMF to FDCA using different nanoparticles as catalysts [2]. For example, Siankevich et al. reported successful oxidation with water-dispersed platinum nanoparticles under gaseous oxygen [49]. In other studies, authors report using supported gold, ruthenium, and platinum nanoparticles with various support systems and reaction conditions [50-56]. Still other studies have reported successfully using bimetallics [57] and earth-abundant metals as catalysts [58, 59]. Another group was able to use copper (I) chloride and 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) radicals as catalysts. It is worth noting that this method did not require a strong base, nor did it produce any toxic metal waste making it particularly attractive [48]. Enzyme catalyzed oxidations utilizing TEMPO-mediated lipase [60] and HMF-oxidase [61] are also shown to produce high yields of HMF. Electrocatalytic oxidation in alkaline media over support gold and palladium nanoparticles was also reported to successfully produce FDCA [62]. As evidenced by the previous examples, there are many ways to oxidize HMF to FDCA. Which method is the most effective and cost efficient for industrial applications, however, is still under debate.



Scheme 2.2 General oxidation mechanism for conversion of HMF to FDCA.

2.2 Liquid Crystal Polymers

There are two known types of liquid crystal polymers (LCPs). The first type is called lyotropic LCPs. These LCPs demonstrate liquid crystalline behavior when dissolved in the appropriate solvents. The second type is called thermotropic LCPs due to their thermally induced liquid crystal behavior present in the melt. Since lyotropic LCPs commonly require expensive and environmentally unfriendly solvents, most research in the field has focused on thermotropic LCPs [63]. Here too, the focus will be on LCPs with thermally induced liquid crystalline behavior. The reader is directed towards Lin et al. [64] and Polk et al. [65] for more detailed information on recent advances in lyotropic LCPs. For a more comprehensive review on both lyotropic and thermotropic LCPs, see Han and Bhowmik's 1997 publication entitled "Wholly Aromatic Liquid-Crystalline Polyesters" [63]. Several other authors have also published in depth reviews of the history of LCPs [66-72]

2.2.1 Wholly Aromatic Polyesters

Research investigating the synthesis and characterization of wholly aromatic polyesters (WAPs) has been well established. Most commonly, these polyesters are crystalline with high melting points (T_m) that tend to be above the degradation temperature [73]. The most common method for synthesizing WAPs is a melt polymerization, also known as a melt polycondensation reaction, a transesterification, or acidolysis. Regardless of the name, this method typically involves reacting the diacetate derivative of an aromatic diol with an acetoxy aromatic acid and/or an aromatic dicarboxylic acid [63]. Initially, research on WAPs explored homopolyesters. What scientists found was that these polyesters posses a high crystal to liquid crystal (LC) transition temperature that is often

too high for reasonable industrial applications, or so high that it cannot be accessed before the polymer degrades [74, 75]. Gilkey and Caldwell were some of the first researchers to investigate the effects of copolymerization. Their published work described their findings on the copolymerization of the meta- and para-hydroxybenzoic (p-HBA) acid isomers. In their results, they reported that higher concentrations of the para substituent resulted in block formations due to the higher reactivity of the para isomer over the meta isomer. When the concentration of the p-HBA were greater than 55%, the block formations resulted in a greatly increased the T_m and caused the polymer to be insoluble in most solvents. When the concentration of the m-HBA was 55% and above the polymer was soluble in multiple solvents. These findings suggested that the characteristics and thermal behavior of a polymer can be manipulated through conformational changes. [76-78] And indeed, it is now understood that there are several structural modifications that can be implemented to lower the T_m. These modifications include copolymerizing mesogens of different shapes and sizes thereby decreasing the overall symmetry, adding bulky substituents to one or more of the monomers, adding spacers like methylene and oxyethylene to increase flexibility in the backbone, introducing non-coplanar monomers such as 2,2 or 4,4-substituted biphenols to reduce chain interactions, and including kinked or bent monomers to lower the persistence length in the LC phase and to disrupt lateral interactions in the solid phase [63, 79-85].

Early investigations into the effects of these structural modifications focused on using substituted benzene, biphenyl, or naphthalene derivatives to disrupt a poly (p-oxybenzoate) backbone. This disruption forms a non-periodic layer adjacent to the crystalline lattice, decreasing intermolecular interactions and thereupon lowering the T_m

[79]. A 1972 US patent by Cottis et al demonstrated this effect by reporting a lower glass transition temperature (Tg), a lower T_m, and a lower crystal to LC transition temperature in copolyesters than in homopolyesters [86]. Following this patent, several other US patents also cited the successful synthesis of wholly aromatic thermotropic copolyesters with more accessible T_m and T_g [87-89]. Unlike homopolymerization, copolymerization results in both head to head and head to tail chain orientations, allowing for a greater amount of free volume and therefore, a lower T_g and T_m [63].

Some researchers have investigated the effects of different substituent structures on the LC phase. As Lenz explains, steric hinderence increases separation in the polymer backbone while molecular interlocking decreases the chain mobility in the mesophase [90]. As such, the shape of the substituent directly impacts the behavior of the polymer in the melt. An example of these effects are seen in a Celanese patent from 1978 that reported the synthesis of WAPs with bulky substituents that had T_ms below 300 ˚C and a LC phase at 290 ˚C [91]. Another US patent cited that increased aromatic content was directly proportional to an increased T_m, but that by substituting a chlorine or benzene on the hydroquinone monomer the group was able to lower the melting point. They also found that replacing some of the aromatic mesogens with aromatic rings without coaxial or parallel chain linkages (ex. isophthalic acid (IA)) also depressed the T_m [92]. As demonstrated by these studies, adding substituents to one or more of the mesogens is a verified method for increasing chain mobility and subsequently lowering the T_m.

Incorporating flexible spacers into the polymer backbone is another effective method for lowering the T_m. Roviello and Sirigu were the first to suggest alternating linear mesogens with flexible spacers to decrease the aromatic density and thusly making

the mesophase more accessible [93]. Blumstein et al. also explored the impact of adding spacers by incorporating methylene groups into the main chain of polymers with mesogenic elements [94]. In a later publication, Blumstein et al. expanded their research to understand the "structure-property correlations in some nematic main-chain polyesters" [95]. Similarly, Lenz published a detailed report on the effects of spacer size and length on thermotropic properties. In this same publication, Lenz also discussed the effect of the main chain monomer structure on thermotropic properties. His results demonstrated that shortening the length of the mesogens caused the LC phase to be less stable. Concurrently, he found that decreasing the linearity of the mesogens, for example by replacing hydroquinone with terephthaloyl moieties, also decreased the mesogenic phase stability and thusly the T_m [96]. These results show that not only does the structure of the flexible spacer directly impact the stability of the mesophase, but the structure of the main chain mesogens also influences the thermotropic behavior of the polymer.

Early in LCP research, it was believed that only linear monomers could be used to produce polymers with a mesogenic phase. Researchers were surprised to find, however, that bent core polymers also displayed thermotropic behavior. To further understand the effects of non-linear mesogen structure on thermotropic behavior, several studies have investigated polyesters with a "kink" or "bend" in the main chain. Erdemir et al. studied the synthesis, structure and thermal transitions for a range of polyesters based on poly (p-oxybenzoate-co-phenylene isophthalate) [97]. Dingemans et al. have also done extensive research in this field of bent core LCPs. Their publications characterize the difference between uniaxial and biaxial nematic LCs [98-100] and describe the synthetic and thermal properties of "boomerang," "hockey stick," and "javelin" shaped polymers [101-

103]. This bent core LCP field of study has continued to expand and is now quite expansive [104-110]. What these studies have concluded is that thermal transitions can be controlled through the incorporation of non-linear moieties. It is important to note, however, that non-linear moieties are non-mesogenic and that only the linear monomers display thermotropic behavior.

There are countless non-linear molecules that can be incorporated into LCPs as non-mesogenic moieties. For example, IA and FDCA are both commonly listed as functional non-linear, non-mesogenic monomers for use in polyesters. For these non-linear monomers, a shorter persistence length corresponds to a lower overall T_m. This correlation is convenient in developing methods to manipulate the thermal behavior of a polymer so as to make processing easier and to allow for a more accessible mesogenic phase. Too high of a concentration of the non-linear moiety, however, will result in a complete loss of the liquid crystalline properties [63]. In fact, Lenz reports that the stability of the LC phase is directly proportional to the mesogenic to non-mesogenic unit ratio [90]. Additionally, Kricheldorf and Erxleben demonstrated that the bond angle around the central atom of a non-linear monomer is an important factor in determining the critical concentration threshold at which the thermotropic properties will be lost. Their results show that the larger the bond angle, the higher the concentration of non-linear moiety that can be added while maintaining the LC behavior [111]. Analogously, Cai et al. investigated the effects of replacing aromatic diacid benzene derived monomer units in polyesters with a diacid thiophene counterpart. Their results demonstrated that replacing monomers such as TPA with IA successfully reduced the T_m, but resulted in an ordinary isotropic melt phase. However, upon replacing TPA with the thiophene

counterpart, 2,5-thiophene, the researchers found no discernible critical threshold and concluded that the thiophene moiety was fully compatible with LCPs [112]. These results are consistent with Kricheldorf and Erxleben findings regarding the importance of the bond angle around the main-chain monomers on thermotropic behavior. They are also a clear demonstration that moieties with larger bond angles are more compatible with LCPs.

2.2.2 Five-membered Rings in Thermotropic Polyesters

The use of five-membered heterocyclic rings in thermotropic polyesters is well documented. Pyradazine, thiadiazole, oxadiazole, and imidazole are just a few examples of five-membered heterocyclic rings commonly used in thermotropic polyesters [113]. Their successful incorporation into thermotropic polyesters is largely due to their desirable bond angles. For example, the 148˚ C1-C2-C5 bond angle of 2,5-thiophene (see figure 2.1) was found to be extremely compatible with thermotropic polyesters. FDCA is another five-membered ring of particular interest to researchers due to its structural similarities with TPA and potential for use in the production of biobased polyesters. Like its aromatic counterpart, FDCA has two carboxylic acids attached in opposite directions to the central ring. Structurally, though, the molecules have some slight differences. TA is highly linear with a bond angle of 180˚ between C1-C2/C5-C6 and 179.4˚ between C1-C2-C5/C6-C5-C2 (see figure 2.1) [11]. FDCA, by contrast, has a 129.4˚ angle between C1-C2/C5-C6 and 154.7˚ angle between C1-C2-C5/C6-C5-C2 (see figure 2.1) [114]. Additionally, the inter-atomic distance between the carboxylic acids is much lower in FDCA than in TA at 4.830 Å and 5.731 Å respectively [11]. Due to these structural differences, substituting FDCA for TA in polyester backbones will impact the polymer

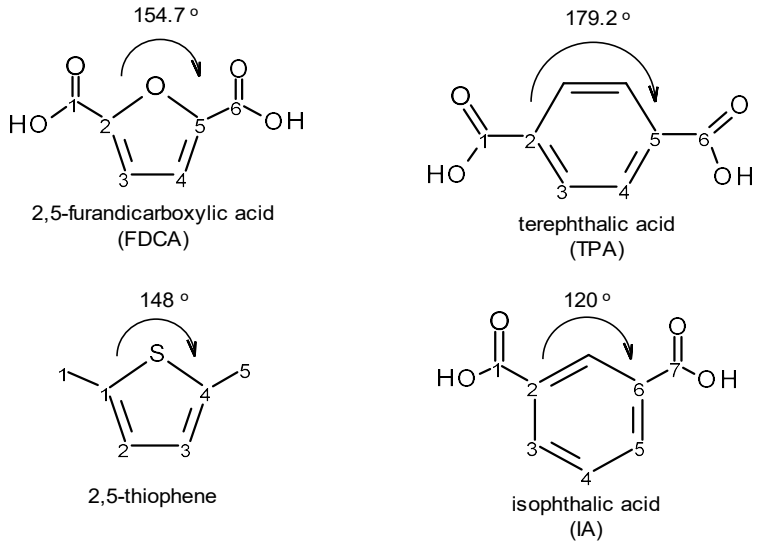


Figure 2.1 Bond angles for cyclic monomers.

by decreasing aromaticity and orientation along the polymer chain and thereby lowering the covalent strength along the chain axis. The two lone electron pairs on the oxygen molecule in the furan ring, however, will increase the overall polarizability of the chain and therefore increase the number of interactions between chains [2]. This internal dipole moment in FDCA will influence the crystallization kinetics and crystalline structure of the LCP [11]. All of these characteristics suggest that FDCA is an ideal moiety for the synthesis of biobased thermotropic polyesters.

2.2.3 Polyesters with 2,5-Furndicarboxylic Acid Moieties

Despite the desirable monomeric characteristics and potential for use in the production of biobased materials, to date, research on thermotropic polyesters with FDCA moieties has been limited. In 2009 a publication by Gandini et al. reported on the synthetic, structural, and thermal properties of homopolyesters poly (1,4-phenylbismethylene 2,5-furancarboxylate) (PHMBF), poly (2,5-furandimethylene 2,5-furandicarboxylate) (PBHMF), and poly (1,4-phenylene 2,5-furandicaroxylate) (PHQF). Their findings

showed that PHMBF was stable up to 300 ˚C with thermal transitions close to PET and PEF. PBHMF was reported as having a low molecular weight (MW) and PHQF was cited as highly crystalline and insoluble in all common organic solvents. Both polyesters were reported to be extremely thermally stable [7].

A couple of recent patents describe the use of FDCA in LCPs. A 1989 Stamicarbon B.V. patent showed that replacing small amounts of TA with FDCA in aromatic polyesters containing two carbonyl groups lowered the T_m while retaining the LC behavior [115]. In 2012 a Japanese patent by Unitika LTD, the inventors successfully produced a LCP by copolymerizing HBA, FDCA and glycol [116]. Around the same time, Wilsens et al. obtained a patent for Teijin Aramid B.V. using FDCA, HBA, any aromatic diol, and an aromatic monocarboxylic acid. As cited by this patent, it is established that FDCA is prone to decarboxylation resulting in the production of CO_2 at reaction temperatures between 220 ˚C and 280 ˚C. It is also established that FDCA is prone to color producing side reactions with the most severe discoloration occurring at 280 ˚C. Additionally, FDCA is shown to decompose at temperatures above 300 ˚C. As such, FDCA derived polymers often have a low MW. For these reasons, the inventors opted to run the polymerization at a lower reaction temperature (230 ˚C) for a longer period of time to try and reduce the production of color and to achieve a higher MW [113]. In a Furanix Technologies B.V. patent, Sipos proposes a multi-step polymerization process to address these challenges regarding MW and color-producing side reactions. This process involves a tin (IV) catalyzed polycondenstation step where FDCA is transesterified with a compound or mixture of compounds containing two or more hydroxyl groups, followed by a solid state polycondensation in the presence of a tin (II)

catalyst to achieve a final polymer with an average MW of at least 10,000 (as determined by GPC based on polystyrene standards) [117]. Regardless of the low MW and color production, these patents were able to successfully synthesize FDCA derived thermotropic polyesters.

Driven by the desperate need to develop biobased polyesters and using the information provided above, this thesis aims to discover a novel, completely renewable sourced thermotropic polyester based on FDCA. In 1994 Makhija and Jaffe published their findings for the synthesis, characterization, and processing of an aromatic copolyester, HIQ, derived from p-HBA, IA, and HQ. They reported that the HIQ polymer synthesized with equimolar proportions of each monomer resulted in a novel polyester with a mesogenic phase. This mesogenic phase, however, was reported to be difficult to access and was quickly lost with even the slightest changes in reaction conditions or monomer concentrations [118]. The carboxylic acid groups in IA form a 120˚ bond angle, while FDCA has a slightly wider angle between its diacids at 154.7˚. Based on the understanding that higher concentrations of non-linear moieties with wider bond angles can be incorporated into polymer backbones to reduce T_m while maintaining LC properties, and the success of recent inventors to produce LCPs with FDCA derivatives, it is proposed that replacing the IA monomer in the HIQ molecule with FDCA will result in a thermotropic polyester with a more accessible mesogenic phase. Additionally, the new polyester, deemed HFQ, will be completely derived from renewable sources.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Materials for 5-Hydroxymethylfurfural Synthesis

The fructose for HMF production was purchased from Sigma-Aldrich (lot# SLBG8126V) and the DMSO was purchased from Alfa Aesar (lot# E25W011). Ethyl acetate for biphase extraction was purchased from Pharmco-Aaper (lot# C1003178). HMF nuclear magnetic resonance (NMR) samples were run in deuterated chloroform with internal tetramethylsilane (TMS) standard obtained from Sigma-Aldrich (lot# MKB129425V).

3.1.2 Materials for 2,5-Furandicarboxylic Acid Synthesis

HMF was synthesized with structure and purity confirmed via NMR spectroscopy as described above. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and sodium bisulfate ($NaHSO_3$) were purchased from Fisher Scientific (lot# 134065, 134172, and 110395 respectively). The potassium permanganate ($KMnO_4$) was obtained from Acros (lot# B0134450). Purity and structure of the final product was determined using NMR spectroscopy in deuterated DMSO from Sigma-Aldrich with TMS internal standard (lot# MKBV1644V).

3.1.3 Materials for Polymerization

For the acetylation of the hydroxyl groups, acetic anhydride was purchased from Fisher Scientific (lot# 137695) and the sodium acetate (NaOAc) catalyst was purchased from Sigma-Aldrich (lot# 041K1615). The FDCA was either synthesized or purchased from

Sigma-Aldrich (lot# MKBS4849V). Purity was determined through NMR spectroscopy with deuterated DMSO with TMS internal standard as the solvent from Sigma-Aldrich (lot# MKBV1644V). Hydroquinone (HQ) was also purchased from Sigma-Aldrich (lot# BLBK0157V). The polymer grade 4-hydroxybenzoic acid (HBA) was a generous gift from Ticona.

3.2 Equipment

All structural conformation and purity data for the synthesis of HMF and FDCA were determined through proton spectroscopy using a Bruker ARX 300 MHz NMR. Polymerizations were carried out in a Techne fluidized bath SBS-4 with a Techne TC-80 temperature control. All thermal data was determined using a Perkin-Elmer differential scanning calorimeter (DSC) 4000 with normal heating and cooling rates of 10 ˚C/min from -20 ˚C to 350 ˚C under a N_2 rich atmosphere. The polymer backbone structure was confirmed with attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) using a Perkin-Elmer FTIR Spectrum 100 fitted with a diamond crystal reflection element. All optical microscopy was performed on a Zeiss West Germany polarizing microscope with Zeiss 40/0,85 pol #4507 08-99 02 lens with a mounted Mettler FP82HT hot stage with a Mettler FP90 central processor.

3.3 Methods

3.3.1 Preparation of 5-Hydroxymethylfurfural

A 500 mL round bottom flask with magnetic stir bar was charged with 0.25 mol of fructose and an 8:1 excess of DMSO. The system was flooded with argon and the reaction was allowed to run for 4 hours at 140 ˚C in an oil bath. The excess DMSO and

water produced from the reaction were evaporated off at 40 ˚C under vacuum using an oil pump. The HMF was then extracted from the resin by adding 300 mL of ethyl acetate and allowing the solution to stir for 2 hours at 50 ˚C. The ethyl acetate solution was then decanted into a new 500 mL round bottom flask and the solvent removed using a rotary evaporator. The purity and structure of the resulting product were confirmed using ^{1}H NMR spectroscopy shown in figure 3.1b with the TMS internal standard peak visible at 0.0 ppm. Figure 3.1a provides a molecular structure diagram showing the protons corresponding to the NMR peaks. These results are in accordance with supporting literature [5]. The general mechanism for this reaction is shown in scheme 2.1.

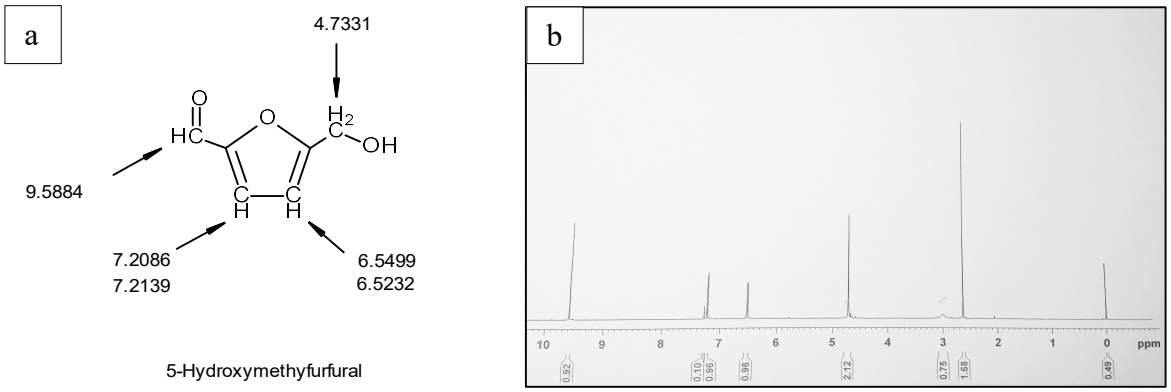


Figure 3.1 a) Molecular structural diagram showing protons with corresponding ppm**.**
b) ^{1}H NMR spectrum for HMF with TMS standard peak at 0.0 ppm.

3.3.2 Preparation of 2,5-furandicarboxylic acid

A 12.5 M solution of NaOH was prepared by adding approximately 1 g of NaOH to 20 mL of distilled water and loaded into a 50 mL round bottom flask with a magnetic stir bar. 1 mmol of HMF (126 mg) was added to the solution. A molar excess of $KMnO_4$ (363 mg) was added to the flask under agitation and the reaction was allowed to continue open to the atmosphere for 20 min. The solution was then acidified by adding concentrated HCl drop wise until the pH was $\leq$ 1. $NaHSO_3$ was then slowly added to reduce the MnO_2, rendering it soluble in the aqueous solution. The solution was then filtered to collect the

precipitated FDCA. The final product was then washed with water and dried in a vacuum oven over night. The general mechanism for this reaction is shown in scheme 2.2. The synthesis and purity of the final product were confirmed using ^{1}H NMR as shown in figure 3.2 which is in agreement with reported data [119].

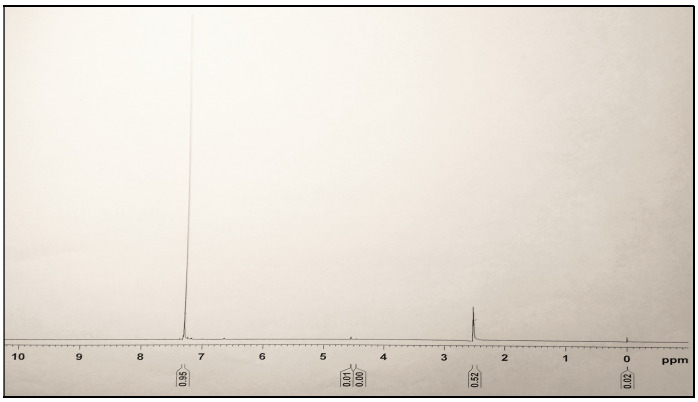


Figure 3.2 NMR spectrum for FDCA synthesis showing FDCA peak at 7. 2889 ppm, TMS standard at 0.0 ppm, and residual DMSO-d_5 in NMR solvent at 2.500 ppm.

3.3.3 Acetylation of Hydroxyl Groups

HQ, HBA, and FDCA were loaded into a test tube in equimolar proportions with a slight molar excess of acetic anhydride, 10 mg of sodium acetate as a catalyst and a magnetic stir bar. Reaction was carried out under argon at 130 ˚C for 90 minutes or until solution had visibly condensed and production of acetic acid stopped. The temperature was then raised to 150 ˚C to distill off excess acetic anhydride. The entire sample was then transferred to the polymerization set up. The structural formulas for the monomers used in the study are shown in figure 3.3.

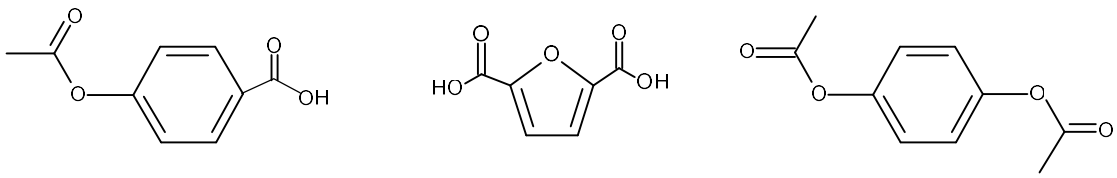
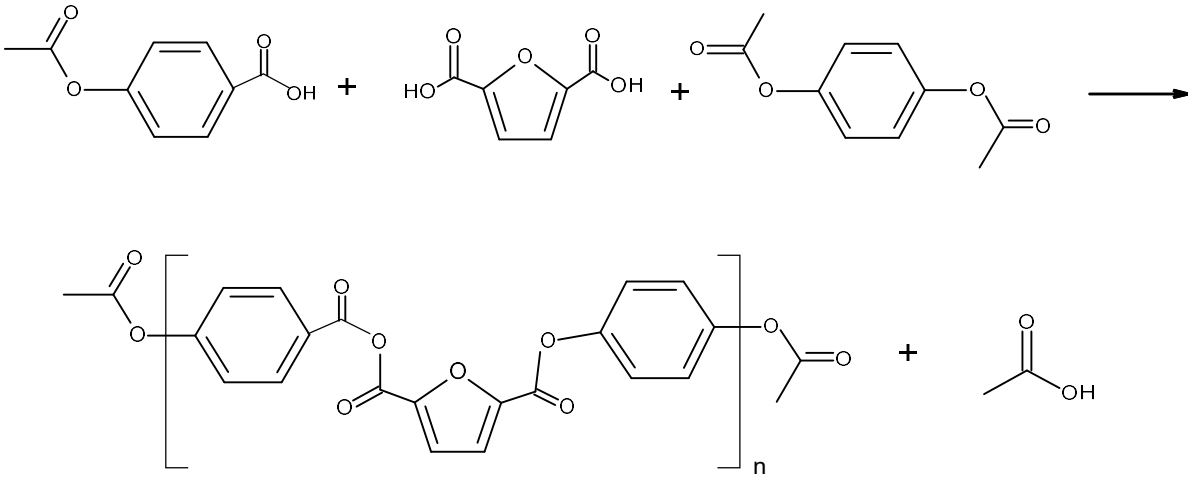


Figure 3.3 Structural formulas for monomers used in this study.

3.3.4 Polycondensation of p-Acetoxybexoic Acid, 2,5-Furandicarboxylic Acid, and Hydroquinone Diacetate

The test tube with the acetylated monomers was placed inside of a polymerization tube with a mechanical stir rod and secured within the polymerization tube with a layer of glass wool to ensure proper mixing. The entire system was placed in a fluidized sand bath. Three argon and vacuum cycles were then performed to remove all oxygen. The system temperature was quickly brought to 170 ˚C and then slowly raised by 20 ˚C every 30 minutes until the reaction temperature of 250 ˚C was achieved. Once condensation commenced vacuum pressure was slowly applied with an oil pump and the reaction was allowed to continue until the melt formed a solid and the condensation of acetic acid stopped. The resulting polymer was then allowed to cool to room temperature and removed from system. The general reaction mechanism for this acidolysis polycondensation is shown in scheme 3.1.



Scheme 3.1 General acidolysis polycondensation occurring in the ABA/FDCA/HQA system. The resulting polymer can be of a random or block nature.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structural and Thermal Analysis

ATR-FTIR spectroscopy was used to analyze the backbone structure of the polymer (see figure 4.1). Samples were prepared by loading a couple of mg of the polymer into a circular mold and heat pressing the sample into a disk. Data was in agreement with reported data for the individual monomers provided by the National Institute of Standards and Technology without, of course, the broad alcohol peaks between 3200 and 3600 cm^{-1} [120].

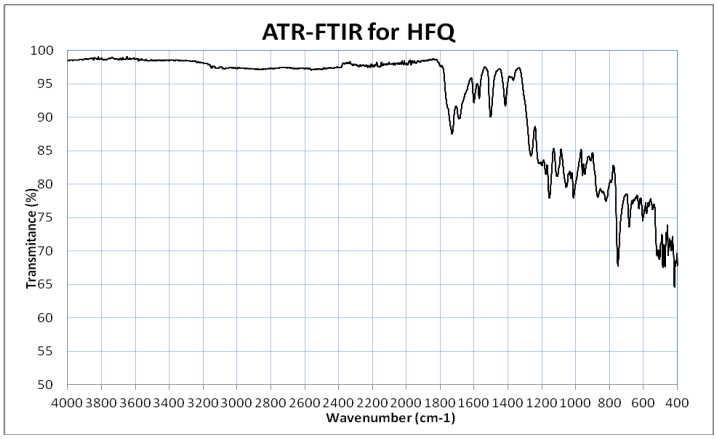


Figure 4.1 ATR-FTIR spectrum of HFQ.

The MW of the final product could not be determined as the polymer was completely insoluble in all known solvents. This insolubility, however, is characteristic of thermotropic polymers with high concentrations of FDCA monomer due to the extended rigid structure of the polymer [7, 63]. This is especially true when the FDCA moieties form large block formations [121]. The overall brittle nature of the polymer, though, indicated a low MW which is also in agreement with reported data on polyesters with

FDCA derivatives. [113, 115, 116, 121] In addition to FDCA's propensity toward side reactions, rapid crystallization, and a high T_m that almost overlaps with the degradation temperature, Wilsens et al. attributed the low MW of FDCA derived polyesters to limited FDCA solubility and reactivity in the melt [79].

The HFQ thermal behavior was analyzed using a DSC spectrum with heating and cooling rates at the normal 10˚ C/min under a N_2 rich atmosphere from -20˚ C to 400˚ C. This spectra is shown in figure 4.2

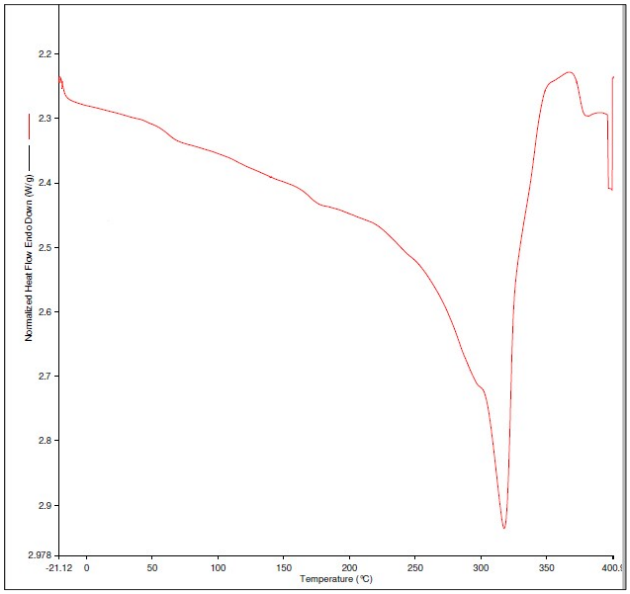


Figure 4.2 DSC spectra of HFQ showing heating cycle with Tg and overlapping crystal to nematic and nematic to isotropic endotherms.

The data indicates a possible T_g around 75˚ C, which seems rather low. Supporting literature, however, states the many thermotropic polyesters have a relatively low T_g that is often lower than non-crystalline polymers, indicating that this is indeed the T_g. Two overlapping T_m endotherms are visible at 300 ˚C with obvious degradation starting at 350 ˚C. LCPs do not generally exhibit polymesomorphism due to high transition temperatures that are above the degradation temperature. This is especially true for wholly aromatic

polymers which only ever demonstrate a nematic mesogenic phase. As such, these endotherms correspond to the crystalline to nematic and nematic to isotropic transition temperatures respectively. It is not unusual for these transition temperature ranges to be so broad that they obscure one another, making detection on DSC difficult. Additionally, it is common for thermotropic polyesters to be biphasic, meaning that the nematic and isotropic melts coexist. This biphasic behavior is due to the incorporation of the non-linear, non-mesogenic FDCA moiety which disrupts the nematic phase so that both the LC phase and isotropic phase are in equilibrium. [63] This thermal data indicates the HFQ is indeed biphasic and is supported by the optical microscopy observations.

4.2 Optical Microscopy

The thermotropic behavior of HFQ was analyzed by observing the behavior in the melt through an optical microscope with crossed polarizers at 400 x magnification. Samples were prepared by loading a mg or less of finely ground polymer onto a glass slide and covering the sample with a glass cover slip. The slide was then inserted into a mounted Mettler FP82HT hot stage attached to a Mettler FP90 central processor temperature control. The sample was observed as the temperature was increased from 30 ˚C to 350 ˚C at a heating rate of 20˚ C/min. Initial observations of the polymer at room temperature under partially crossed polarizers demonstrated that the polymer is highly crystalline (see figure 4.3 a and b). Birefringence and the formation of nematic droplets with Schlieren texture was observed from 270 ˚C to 350 ˚C. This birefringence and texture, however, was not uniform with dark areas indicating a concurrent isotropic melt phase (see figure 4.3 c-e). It is reasonable to consider that these isotropic areas have higher concentrations of FDCA block formations. Additionally, published findings cite that Schlieren texture is

often obscured in random copolyesters as the texture does not coarsen to give the traditional threaded texture [67]. Regardless, the optical observations demonstrate that HFQ is biphasic, displaying simultaneous nematic and isotropic phases.

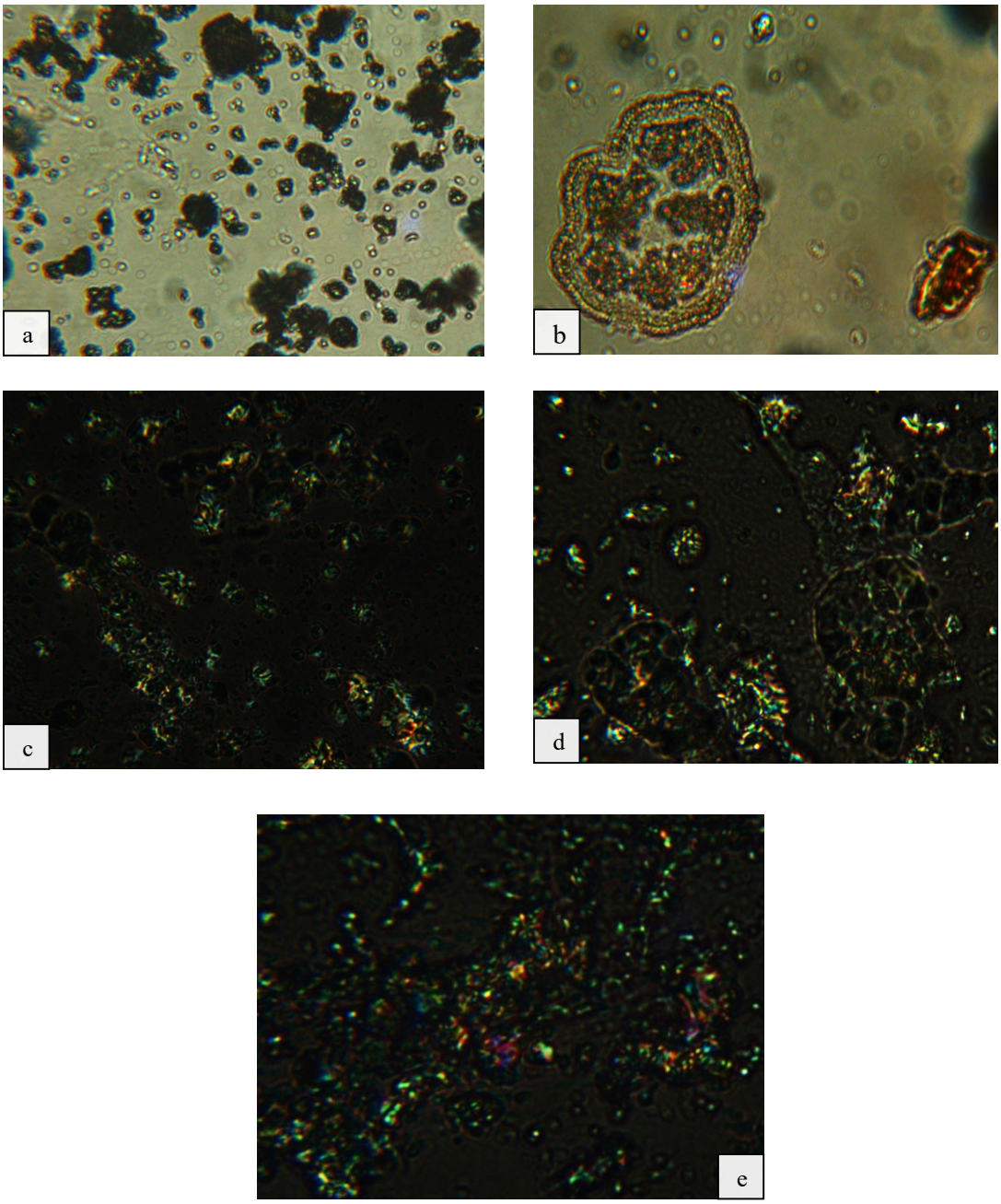


Figure 4.3 a-b) Crystalline structure of HFQ visible at room temperature under partially crossed polarizers at 400 x magnification. **c-e)** Nematic droplets with Schlieren texture in equilibrium with isotropic melt phase at 270-350 ˚C at 400 x magnification.

CHAPTER 5

CONCLUSION

This thesis describes the synthesis of a novel, totally renewable sourced thermotropic polyester, HFQ, derived from p-HBA, FDCA, and HQ. The data reported illustrates the potential for the application of FDCA in developing biobased polyesters to replace traditional non-renewable sourced materials. Challenges still remain in developing a low-cost, environmentally friendly synthetic method for the conversion of fructose to HMF. The exponential increase in researched focused in this area in the last decade, however, has produced promising results that suggest a solution is near. Future considerations would be to develop more efficient polymerization methods that result in a higher MW. Additional considerations would be to explore ways in which to further separate and stabilize the nematic range. HFQ, though, is an excellent starting point for the development of completely biobased polyesters and biomaterials.

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